SYNOPSIS

"Development of Thermoelectric Nanostructured Materials (Undoped and Doped Metal Oxides) for Energy Harvesting Applications"

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Title

Development of Thermoelectric Nanostructured Materials (undoped and doped metal oxides) for Energy Harvesting Applications

1. Introduction:

Over the past decade, there is increasing global energy demand. It is to be fulfilled by way of environmentally and geopolitically sustainable manner, which is one of the most serious technological challenges in front of the scientist. As per the recent IEA report, world total consumption of energy (104,426 TWh) is produced from Oil (40.7 %), Coal/Peat/Shale (10.1%), Natural Gas (15.2%), Biofuels and waste (12.4%), Electricity (18.1%) and renewable (3.5%).[1] Moreover, a large portion of oil energy is utilized for transportation. For example, a vehicle powered by typical petroleum fuelled internal combustion engine, majority of the energy is lost as waste heat and only 25% of the fuel energy is used for vehicle mobility and accessory power.[2,3] Current waste energy assessments indicate that the energy equivalent of 45 billion gallons of oil is wasted annually from the exhaust pipes of ~160 million vehicles in India only.[4] Additionally waste heat is generated from household equipments to electrical power generating plants and manufacturing industries. Therefore, there is urgent need for harvesting the waste heat in an efficient, economical, and environment friendly manner. The high efficiency thermoelectric materials that convert waste heat directly into electricity are promising to fulfill this need.

The conversion efficiency of thermoelectric materials is related to a quantity called as figure of merit (ZT) and is governed by electric and thermal transport properties of those materials.[5] The thermoelectric effect is a material property that exists in all materials but some materials have high ZT. Examples of such materials are Bi_2Te_3, PbTe, $CoSb_3$, SiGe, PbTeSe, Sb_2Te_3, etc. which have high ZT in the range of 0.8 to 2.4 under working temperature range from 200 to 800 ^{o}C.[6,7] This significant enhancement in the efficiency is due to high electric conductivity and low thermal conductivity of these materials. In normal materials, this turns out to be rather challenging, because high electric conductivity is usually accompanied by high thermal conductivity of that material. Recent strategies to improve thermoelectrics include both advanced bulk materials and the use of low-dimensional materials. Such approach reduces thermal conductivity via reducing phonon contribution due to their substantially increased interfaces, which eventually enhances

electrical conductivity of the device resulting in high ZT.[5] Moreover, superlattices of these materials are also considered a good candidate for better thermoelectric device manufacturing but the production is bit high.

Despite such a high anticipation and achievements, the progress in the thermoelectric materials has still been limited to those current thermoelectric materials for practical applications. Therefore, there is a great potential to seek new technology and materials with higher ZT values to provide the desired conversion efficiencies.

2. Review of Literature and Development in the Subject:

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. In the 1950s, alloys of BiTe, PbTe, SrTe, SnSe, SnSe, etc.[8-12] were discovered to produce thermoelectric effects and played a vital role in the field of thermoelectrics. Despite these attractive results, for instance, does not seem to be utilized for real-life applications since it has displayed its high ZT only along one crystallographic direction at high temperature.

To solve these problems, novel thermoelectric materials with high ZT composed of nontoxic, naturally abundant, light, and cheap elements should be developed. Metal oxides possess these requirements, and they are highly promising candidates from this point of view. Among metal oxides, crystalline SnO_2, TiO_2, ZnO, etc. are attractive materials for waste heat recovery, particularly at high temperatures[13-15].

Focuses in this case is mainly on binary metal oxides and doped related oxides. From the point of view of the electrical conductivity and carrier mobility, transparent conductive oxides have potential for thermoelectric applications.

3. Objectives of Research/ Proposed Hypothesis:

This work proposes efficient method for synthesis of low dimensional thermoelectric materials (Undoped and Doped Metal Oxides) for energy harvesting from waste heat of any

system. The basic concept of thermoelectric effect is that the thermal strain applied on to the material converts it into electrical energy. It is very reliable to use thermoelectric materials for generating electrical energy which can be used for powering any portable devices. In the present day scenario, wherein there is great demand for energy, this idea of thermoelectric concept works well.

This work will investigate device properties of metal oxide thin films synthesized using sol-gel assisted spin coating technique. To achieve the above mention objective this work is made of specific aims

a. To synthesize metal oxide thin film and nanostructure on substrate using sol-gel technique.
b. To characterize synthesized thin films and nanostructure using XRD, UV-Vis spectroscopy, Raman spectroscopy, TGA-DTA, SEM-EDS, XPS, etc.
c. To study the electrical conductivity and carrier mobility, transparent conductive properties of thin films and nanostructures using dedicated electrical characterization setup.
c. To probe the electronic structure of the film using X-ray photoelectron spectroscopy and understanding the role of its intrinsic properties on charge transport.
d. To propose effective device based on the results and material properties.

4. Methodology to be adopted:

The work predicted under this plan involves efforts on several different aspects and their integration in the interest of a desired property response and/or device action. The work elements can be broadly categorized under four classes namely materials synthesis, film growth, processing and characterization, although the processing and growth aspects could be employed interchangeably depending on the nature of the desired film. In terms of a plan definition, the following activities/effort elements can be presented, however, the specificity could evolve dynamically depending on the success or failure of a particular approach and the need to modify or steer the same.

Activity 1: Employing physical / chemical (sol-gel) routes for synthesis of nanostructured material of interest*:* This will involve synthesis of thermoelectric material (undoped and doped metal oxides) via physical or chemical routes with various specifications. In this domain the in-house efforts will be complimented and enriched to synthesize of gel,

emphasizing homogeneity and narrow property distributions so as to explore the possibility of potential technological fall outs.

Activity 2: Post processing of the nano-structured material: The next step will be to achieve physico-chemical integration of the nanosystems and the underlying film configuration, to generate a new/novel response specific to the hybrid aspect of the coupled system. This may involve low temperature annealing/sintering, radiation sintering or overgrowth to embed the self assembled structure.

Activity 3: Characterization: Employing a broad based characterization manifold is key to both, the process parameter optimization for the growth of specific configurations and elucidation of the property features realized in such hybrids. It will of course be important to separately characterize the films and the nanosystems for their quality and property optimization. The characterization techniques which will be liberally employed will include x-ray diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), optical spectroscopy, Raman spectroscopy, x-ray photoelectron spectroscopy (XPS0), etc.

Activity 4: Device actions explorations: The device action categories for which the nano-film hybrids will be examined include the seebeck coefficient, electrical resistivity, thermal conductivity and thermoelectric figure of merit ZT. A series of repetitive thermoelectric measurements will reveal a substantially enhanced thermoelectric figure of merit ZT.

5. Importance of study/ Society applications:

National status:

Numbers of research groups across country are working on this important issue of thermoelectric materials and the outcomes addressing a variety of issues in this field have been supported by Government of India. Although it is difficult to summarize the whole effort, a representative cross section of ideas and strategies can be provided as follows: Dr. Ajay Soni (IIT, Mandi), Dr. Chandan Bera (INST, Mohali), Dr. U. V. Varadaraju (IIT, Madras), Dr. Kanishka Biswas (JNCASR, Jakkur), Prof Somaditya Sen (IIT, Indore), Dr. Satishchandra B. Ogale (IISER, Pune), etc.

International status:

In the specific research area to be focused upon in the proposed project, the international research is just beginning to grow creating a fairly open opportunities for Indian science to take a lead and make a substantial impact. These developments are occurring in the domains of new device concept such as non-volatile memory. Few impressive examples who flourish the focus of this project are: Dr. Mercouri G. Kanatzidis (Northwestern University, USA), Dr. G. Jeffrey Snyder (California Institute of Technology, USA), Dr. Kim Sung–woong (Sungkyunkwan University, Korea), etc. Many more internationally reputed scientists published lots of literature in research journals like: Nature, Science, Advanced Materials, Nano Letters, Advanced Functional Materials, etc.

Significance of the study:

As stated earlier, this work aims to make a modest contribution to the highly desirable goal of being able to bridge the wide gap between exciting energy harvesting and usable technology, especially in the high technology domain. It focuses on the issue of energy harvesting where a large amount of energy produced just using oil is lost on daily basis. This platform emphasizes synergetic integration with potential for novel effects exclusive to the hybrid concept for thermoelectric energy harvesting.

6. Proposed work Plan/Formation and Structure of Study: Year-wise Plan of work and targets to be achieved:

First Year:

a. Initiate sol-gel synthesis of undoped metal oxide thin films and nanostructures
b. Initiate and optimize solution based thin film growth methods (spin coating) for functional oxide coatings.
c. Study effect of temperature on film morphology.
d. Perform extensive in-house characterizations including UV-Vis, XRD, AFM, TGA, etc. as well as those involving external collaborations SEM-EDS, TEM and XPS to know the structural, optical, thermal and electronic properties of synthesized thin film.

Second Year:

a. Establish and implement characterization strategies for the films and the nano-film hybrids.
b. Initiate testing of device properties of undoped metal oxide films.
c. Initiate and optimize sol-gel technique for doping of functional oxide with metal.
d. Initiate and optimize thin film growth methods (spin coating) for doped functional oxide coatings on various substrates.

e. Study effect of temperature and doping concentration on film morphology.

Third Year:

a. Perform extensive in-house characterizations including UV-Vis, XRD, AFM, TGA, etc. as well as those involving external collaborations SEM-EDS, TEM and XPS to know the structural, optical and electronic properties of synthesized thin film.
b. Test of device properties of doped metal oxide films.
c. Start publishing research papers.

Fourth Year:

a. Review the status of progress during the first two years and to take appropriate steps towards the most effective utilization of the knowledge, facilities and experience during the remaining duration.
b. Continue to analyze the data obtained and proceed with publications/patenting as appropriate.
c. Conduct meetings with industry and national laboratory personnel to explore application avenues.
d. Prepare thesis for submission.

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